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Steam cracking of renewable feedstock: ab initio based modeling of thermochemistry

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INTRODUCTION

To optimize current technology and design new processes, models of the underlying chemistry are required. Most kinetic models require many thermochemical and kinetic data, which are difficult to obtain experimentally. As computer programs evolve and the computational capabilities of computers increase, it has become feasible to acquire accurate data for almost all types of chemical compounds using computational chemistry.

COMPUTATIONAL METHODOLOGY

Ab initio calculations

- Geometry optimization using HO statistical thermodynamics based on B3LYP/6-311G(d,p) method.
- CBS-QB3 multicompound methodology with 1D-HR corrections used for energy calculations based on optimized geometries.
- HSCP1 program for identification of internal rotors (program developed in LCT)
- Calculations of the energy profiles for the internal rotations using B3LYP/6-31G(d) method.
- HSCP2 program for applying internal rotor corrections to the thermodynamic properties (program developed in LCT)

Benson's Group Additivity Method

Due to the insufficiency of the method to account for all interactions present in one molecule also non-nearest-neighbor interactions (NNIs) are accounted for by adding NNI corrections.
The group additive values and corrections for non-nearest-neighbor interactions (NNI) are determined simultaneously by unweighed least-square analysis and finally. To assess the reliability of the group additivity approximation, a statistical analysis is performed.

$$f = \sum_i GAV_f(\text{group}_i) + \sum_j NNI_j$$

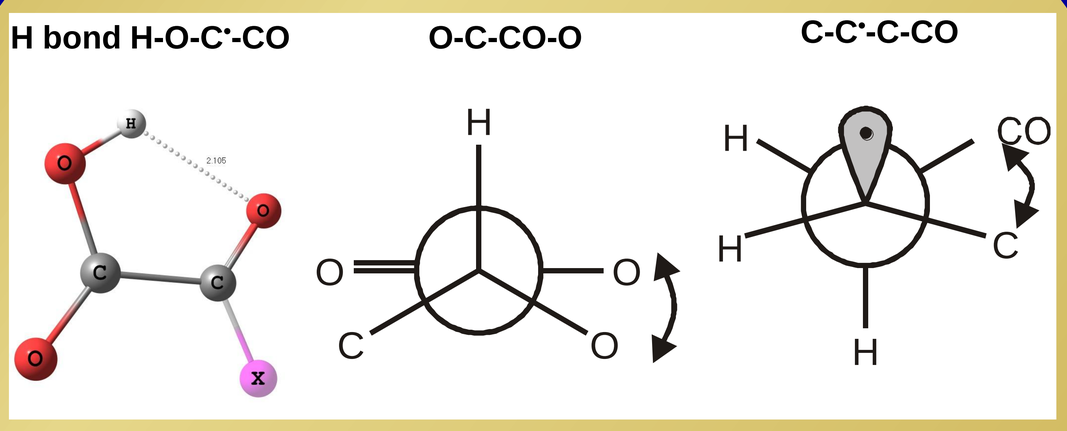
Group additive values (**GAV**)

Corrections for non-nearest-neighbor interactions (**NNI**)
- ✓ hydrogen bonds
- ✓ gauche interactions
- ✓ other interactions

$$f = \Delta_f H°, S°_{int}, C°_p \qquad S°_{int} = S° + R\ln\left(\frac{\sigma}{n_{opt}}\right)$$

EXAMPLES OF NNIs

H bond H-O-C•-CO | **O-C-CO-O** | **C-C•-C-CO**



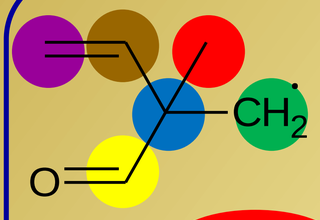
$\Delta_f H°$ (298 K)	$S°$ (298 K)	$C_p°$ (300 K)
-22.79	-16.5	-3.86

$\Delta_f H°$ (298 K)	$S°$ (298 K)	$C_p°$ (300 K)
0.42	-3.62	0.91

$\Delta_f H°$ (298 K)	$S°$ (298 K)	$C_p°$ (300 K)
6.49	2.21	-4.97

✓H bonds are stabilizing interactions ─ gauche interactions have the opposite effect
✓ there is a decrease in the internal flexibility of the molecule or radical
✓ hydrogen bonds are on the edge of group additivity: difficult to model but with a large contribution to thermochemistry

EXAMPLE OF GA SCHEME



Firstly, Benson's GA groups identified, the sum of their values for the particular thermochemical property $\Delta_f H°$, $S°$ or $C_p°$ gives the corresponding thermochemical property of the molecule or the radical.

$\Delta_f H°$= GAV[C–(C)(H)$_3$] + GAV[CO–(C)(H)] + GAV[C°–(C)(H)$_2$] + GAV[C–(C$_d$)(C°)(C)(CO)] + GAV[C$_d$–(H)$_2$] + GAV[C$_d$– (C)(H)]

RESULTS

GAV-NNI estimation

Entire training set
202 molecules
248 radicals

→

NNI corrections
15 NNIs for molecules
13 NNIs for radicals

+

GAVs calculated
59 GAVs for molecules
97 GAVs for radicals

Validation of the group additive scheme

Deviation between group additive prediction (GA) and ab initio values (AI): GA−AI

	$\Delta_f H°$ (298 K)	$S°$ (298 K)	$C_p°$ 300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
MAD	2.4	3.8	2.6	2.5	2.2	2.0	1.8	1.4	1.1
RMS	2.9	4.2	3.3	3.0	2.7	2.6	2.3	1.9	1.5
MAX	6.4	7.1	6.1	6.0	6.0	5.9	5.7	5.0	3.8

Deviation between group additive prediction (GA) and experimental values (AI): GA−EXP

	$\Delta_f H°$ (298 K)	$S°$ (298 K)	$C_p°$ 300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
MAD	4.4	0.5	–	2.1	1.9	–	–	–	–
RMS	5.8	0.7	–	2.5	1.9	–	–	–	–
MAX	14.67	1.2	–	4.6	1.9	–	–	–	–

Table 1: Comparison between GA and AI values for the validation set of 11 molecules and 11 radicals, and between GA and experimental values taken by NIST webbook [1]. (MAD: mean absolute deviation, RMS: root mean square deviation, MAX: maximum deviation). $\Delta_f H°$ in kJ/mol, $S°$ and $C_p°$ in J mol^{-1} K^{-1}.

CONCLUSIONS

- The agreement of group additive predictions with ab initio and experimental values means that the GAVs reported in this work can be reliably applied for the prediction of thermochemical data for large oxygenate compounds.
- The group additivity values obtained in this study substantially augment the current database of groups for estimating thermodynamic properties, in particular for oxygenate radicals.

REFERENCES

[1] C.W. NIST, NIST Standard Reference Database Number 69, June **2009**.
[2] M.K. Sabbe, F. De Vleeschouwer, M.F. Reyniers, M. Waroquier, G.B. Marin, J Phys Chem A 112 (**2008**) .
[3] M.K. Sabbe, M. Saeys, M.F. Reyniers, G.B. Marin, V. Van Speybroeck, M. Waroquier, J Phys Chem A 109 (**2005**) .
[4] R. Sumathi, W.H. Green, J Phys Chem A 106 (**2002**) .
[5] S.S. Khan, X.R. Yu, J.R. Wade, R.D. Malmgren, L.J. Broadbelt, J Phys Chem A 113 (**2009**) .
[6] B.E. Poling, J.M. Prausnitz, J.P. O'Connel, The properties of gases and liquids, McGraw-Hill, New York, **2001**.

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